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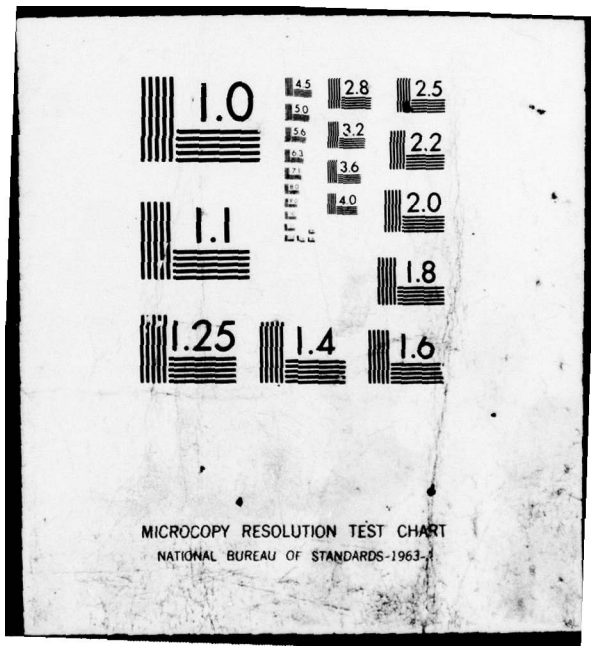
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PICOSECOND RADIATIONLESS TRANSITIONS IN POLYATOMIC MOLECULES

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FINAL TECHNICAL REPORT

LEVEL II

G. WILSE ROBINSON

10 MAY, 1979

U. S. ARMY RESEARCH OFFICE

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LUBBOCK, TX. 79409

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

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2. photochemistry
3. picosecond laser spectroscopy
4. nonexponential decay

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Picosecond laser spectroscopy presents the best experimental methods for studying radiationless transitions in polyatomic molecules, a long time interest of the author and supported mainly by past ARO grants and/or contracts. This final report summarizes some work in picosecond laser spectroscopy, much of it preliminary, carried out during the termination phase of ARO research support.

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Body of Final Report

SUMMARY OF RESEARCH RESULTS:

The Final Report dated 19 May 1977 (California Institute of Technology) for the period 1 February 1974 to 31 January 1977 should be consulted to obtain a complete picture of the results of ARO supported work in the areas of radiationless transition theory and picosecond laser spectroscopy. During 1974-1975, eight papers were published under this contract. In the period 1976-1977 six additional papers were published under Grants DAAG29 76 G 0289 and DAAG29 77 G 0028. Those papers are listed in this final report.

During the brief grant period at Texas Tech, a number of laser innovations were successfully made and a number of applications of picosecond pulse spectroscopy were begun. The mode-locking dye solvent, dichlorethane, was found to improve through purification on a superactive alumina column. The dye solution is continuously pumped (about 5 drops/sec) through the dye cell in the laser cavity, and a 0.02 micron pore-size filter is placed in series with the dye cell. This procedure greatly improves laser reliability. A flat-flat oscillator rod, each end anti-reflectance coated for the 1.054 μ laser output, was found to be a great improvement over the Brewster-Brewster configuration. The need for time-consuming daily laser line-up for good mode-locking with the B-B configuration is now totally absent.

Preliminary experiments on xanthene and merocyanine dyes were carried out. In the case of merocyanine 540 a feasibility study showed that detection of the subnanosecond fluorescence decay of this interesting molecule is well above noise level. While nothing unusual was observed, the presence of dimers in nonpolar solvents and a supposed change of lifetime with electric field strength were two interesting aspects that were to have been followed up.

Highly polar xanthene dyes have two strongly absorbing singlet states in the U.V. -visible regions separated by a large energy gap. The radiationless process connecting these two states was studied. Excitation into the second singlet with a $\lambda = 264$ nm (ultraviolet) picosecond pulse and observation of the fluorescence at about 600 nm in a very preliminary experiment showed a risetime less than 15 psec. A hint of a risetime was apparent, but improved time resolution would be required for a definitive result. Nonpolar molecules with a large energy gap, azulene being the classic example, may have a propensity for slower $S_2 \rightarrow S_1$ nonradiative transitions than these polar molecules. Finally, relaxation and solvent-solvent energy transfer in a large number of systems was under study at the time of termination of the grant. The latter study now seems to be leading to a new formulation of diffusion controlled chemical kinetics at early times. It was hoped also that studies of polymer motions on the molecular scale could be made by using fluorescence probe molecules attached to various positions in the polymer.

PERSONNEL SUPPORTED BY GRANT:

Dr. Thomas A. Caughey (Ph. D., Madison)
January, 1976 ——— April, 1978

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